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Requested Patent GB422488A
Title: PROCESS OF PRINTING TEXTILE MATERIALS ;
Abstracted Patent GB422488 ;
Publication Date: 1935-01-14 ;
Inventor(s): ;
Applicant(s): IG FARBENINDUSTRIE AG ;
Application Number: GB19330019979 19330714 ;
Priority Number(s): DEX422488 19320714 ;
IPC Classification: ;
Equivalents: ;

ABSTRACT:

Printing.—Pattern effects are produced upon textile materials by printing thereon a paste containing a mixture of a substantive azo component free from sulphonie or carboxylic acid groups, sufficient alkali to dissolve this component, a water-soluble diazoamino compound, a resist to ester salts of leuco vat dyestuffs such as an oxide, hydroxide or carbonate of zinc, an alkaline earth metal or magnesium, and, if desired, a small quantity of a mild reducing agent, thereupon over-printing in a different pattern with a paste containing an ester salt of a leuco vat dyestuff, an oxidizing agent, e.g. sodium chlorate, an oxidation accelerator, e.g. ammonium vanadate, and an agent yielding a non-volatile acid, e.g. diethyl tartrate or an ammonium salt or an easily dissociating metal salt of such an acid, e.g. ammonium thiocyanate, glycollate, oxalate, lactate, citrate or tartrate or a sulphate of magnesium, zinc or aluminium, and thereafter steaming, washing and soaping the materials. Alternatively, an aniline black or like preparation and a resist therefor, such as an oxide, hydroxide or carbonate of zinc or manganese, may be substituted for the ester salt of a leuco vat dyestuff and its resist, respectively, with the substitution, if desired, for the agent yielding a non-volatile acid in the over-printing paste, of a free non-volatile organic acid or a feeble non-volatile inorganic acid, e.g. phosphoric acid. Further effects are obtainable by printing, in a separate pattern or in admixture with the diazoamino compound preparations, either mixtures of alkali metal salts of aromatic nitrosamines with substantive azo components or preparations containing vat dyes to be developed by the formaldehyde sulphonylate process. Specified substantive azo components are naphthols, pyrazolones, arylides of 2 : 3-oxynaphthoic acid or of *b* -ketocarboxylic acids such as acetoacetic, benzoylacetic or terephthaloyldiacetic acids, e.g. diacetoacetylbenzidine or diacetoacetylolidine, and arylides of 2 : 3-oxanthracenecarboxylic acid, *o*-oxycarbazolecarboxylic acids or *o*-oxybenzocarbazolecarboxylic acids. The water-soluble diazoamino compounds may be those of Specifications 320,324 and 329,353, [both in Class 15 (ii)]. The following examples are specified. (1) White cotton goods are printed with an aqueous paste containing alcohol, caustic soda, starch tragacanth thickening, zinc white, sodium thiosulphate and a dyestuff preparation (cf. Specification 334,529, [Class 15 (ii)]) consisting of a mixture of the sodium salt of the *o*-toluidide of 2 : 3-oxynaphthoic acid with the diazoamino compound from 5-chloro-2-methyl-1-aminobenzene and 4-sulpho-2-aminobenzoic acid, the goods are dried and over-printed with an aqueous paste containing ethylenethiodiglycol, starch tragacanth thickening, ammonia, glycollic acid, ammonium thiocyanate, sodium chlorate, ammonium vanadate and the sodium salt of the sulphuric acid ester of leuco-5 : 7 : 5 : 7-tetrabromindigo and the over-printed goods are dried, steamed for 5 minutes, rinsed and soaped at the boil; the over-printed parts of the first printed pattern are red and the remaining over-printed parts are blue. (2) The goods are printed with aqueous pastes side by side, containing (a) alcohol, caustic soda, starch tragacanth thickening, zinc white, sodium thiocyanate and a mixture (cf. Specification 334,529) of the sodium salt of the 2-toluidide of 2 : 3-oxynaphthoic acid with the diazoamino compound from 3-chloraniline and 4-sulpho-2-aminobenzoic acid; (b) alcohol, caustic soda, starch tragacanth thickening, zinc white, magnesia, sodium thiosulphate and a mixture of the sodium salt of the anilide of 2 : 3-oxynaphthoic acid with the diazoamino compound from 1-amino-2-methoxy-4-benzoylamino - 5 - methylbenzene and sarcosine, the printed goods are dried and over-printed with an aqueous paste similar to the over-printing paste in (1) containing as the dyestuff the sodium salt of the sulphuric acid ester of leucodimethoxydibenzanthrone, and the over-printed goods are steamed for 5 minutes, rinsed and soaped at the boil; the over-printed parts of patterns (a) and (b) are vivid orange and violet respectively and the remaining over-printed parts are green. (3) The goods are printed with aqueous pastes side by side

RESERVE COPY PATENT SPECIFICATION



Convention Date (Germany): July 14, 1932.

422,488

Application Date (in United Kingdom): July 14, 1933. No. 19979/33.

Complete Specification Accepted: Jan. 14, 1935.

COMPLETE SPECIFICATION

Process of Printing Textile Materials

We, I. G. FARBENINDUSTRIE AKTIEN-GESELLSCHAFT, a Joint Stock Company organised according to the laws of Germany, of Frankfurt a/Main, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 Hitherto, conversion effects have been produced, for instance, by printing different mordants on a white material and then over-printing with a mordant-dye yielding a different shade with each mor-
15 dant. By subsequently steaming, different shades were obtained at the places where the pattern produced by the mordant-printing roller came in contact with the pattern of the over-printing roller.
20 This process, however, allows a very limited number of combinations, since by means of a mordant dye only a small number of tints can be obtained. Moreover, the prints produced by means of
25 mordant dyes do not fulfil in all cases the requirements with respect to fastness.

According to this invention beautiful conversion effects of a great variety of shades and combinations may be produced
30 by printing first with an azo-dyestuff preparation comprising a substantive azo-component and a water-soluble diazo-amino-compound and over-printing with an ester salt of a leuco-vat-dyestuff or
35 with an aniline black—or a similar preparation, the process being conducted in the following manner:—

A pattern is printed with use of a printing paste which contains besides the usual
40 thickening agent and the mixture of a substantive azo-component with a water-soluble diazo-amino-compound, a quantity of alkali necessary for dissolving the dyestuff component and an agent which
45 acts as a resist to the ester salt of the leuco-vat-dyestuff, such as an oxide, a hydroxide or a carbonate of zinc or of an alkaline earth metal or of magnesium, and, if required, a reducing agent of mild
50 action, such as, for instance, sodium thio-sulphate. Another pattern is then over-printed with use of a printing paste which contains an ester salt of a leuco-vat-dye-

stuff, an oxidising agent, such as sodium chlorate, an agent that yields a non-volatile acid, for instance an ammonium salt of a non-volatile acid, such as thiocyanic acid, glycollic acid, oxalic acid, lactic acid, citric acid or tartaric acid, or diethyltartrate or the like, or an easily dissociating metal salt of a non-volatile acid, such as, for instance, a sulphate of magnesium, zinc, aluminium or the like, or a mixture of the said substances which yield non-volatile acid and furthermore an oxidation accelerator, such as ammonium vanadate. The material thus printed is then steamed.

On steaming, there is developed, at the places where the pattern of the first-printing roller comes in contact with the pattern of the over-printing roller, by means of the agent or agents that yield acid, the corresponding insoluble azo-dyestuff from the mixture used for the first print, but the ester salt of the vat-dyestuff is reserved at these places, whereas at those places where the pattern of the over-printing roller has no contact with the pattern of the first printing roller the vat-dyestuff is formed from the ester salt. On the other hand, at those parts of the first printed pattern which have not been over-printed with the ester salt printing colour, that is to say, where the pattern of the over-printing roller does not cover that of the first-printing roller, the mixture of the diazo-amino-compound and the azo-component remains undeveloped, even on steaming, and can later be removed by a suitable washing process so that these places of the material remain white. In other words: After washing and soaping at the boil the pattern of the over-printing roller appears at the first printed parts in the colour of the insoluble azo-dyestuff developed from the paste first printed, and at the not pre-printed places in the colour of the vat-dyestuff developed from the over-printed ester salt, whereas the not over-printed parts of the first printed pattern remain white.

Since all mixtures of water-soluble diazo-amino-compounds with substantive azo-components, and all ester salts of leuco-vat-dyestuffs may be used in the

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above described manner for the preparation of conversion effects, the possible combinations are manifold. This constitutes a great advantage in finishing textile goods; so large a variety of colour and richness of design could not be obtained by means of the known processes. Since it is possible to print simultaneously and side by side mixtures of different diazo-amino-compounds with different azo-components and to over-print, also side by side, ester salts of different vat-dyestuffs, still more variations may be obtained. Further, new effects can be produced by printing in a separate pattern or in admixture with the aforesaid pastes containing mixtures of diazo-amino-compounds and substantive azo-components, which are only developed at the over-printed parts, mixtures of alkali metal salts of aromatic nitrosamines and substantive azo-components, or vat-dyestuffs to be developed according to the potash-sodiumsulphoxylate-formaldehyde process. The preparations from the two last mentioned groups of dyestuffs are then developed, on steaming, throughout the whole of the pattern in which they are printed.

Instead of ester salts of vat dyestuffs there may be used in an analogous manner aniline black or similar preparations for producing over-printed patterns. In this case there is first printed the mixture of water-soluble diazo-amino-compound and substantive azo-component containing a quantity of alkali necessary for dissolving the said component and also a suitable resist to the aniline black preparation, such as an oxide, a hydroxide or a carbonate of a heavy metal, such as zinc, manganese or the like, and, if required, a small quantity of sodium thiosulphate; the material is then over-printed with the aniline black preparation with addition of a non-volatile organic acid, for instance, glycollic acid, tartaric acid, lactic acid, oxalic acid, citric acid or a weak non-volatile inorganic acid, such as, for instance, phosphoric acid, or another of the aforesaid substances which yield non-volatile acids or mixtures thereof. At the first printed places the aniline black is reserved on subsequently steaming and, at the same time, the mixture of water-soluble diazo-amino-compound and substantive azo-component is developed to the corresponding water-insoluble azo-dyestuff, whereas the aniline black is developed on those places where the pattern of the over-printing roller has no contact with the pattern of the first printing roller.

In a similar manner to that described above for the over-printing with the leuco-

ester salt preparation, mixtures of alkali metal salts of nitrosamines with azo-components, or vat-dyestuffs to be developed by the potash-sodium-sulphoxylate formaldehyde process, may also be used in the last-mentioned modification of the new process in which an aniline-black preparation is over-printed, the aforesaid nitrosamine or vat-dyestuff printing preparation being printed in a separate pattern or used in admixture with the preparations containing mixtures of diazo-amino-compounds and substantive azo-components. In this case, the dyestuffs from the two last-named preparations are developed, on steaming, throughout the whole of the pattern in which they are printed. It is also possible to use mixtures of water-soluble diazo-amino-compounds with substantive azo-components simultaneously with ester salts of vat-dyestuffs for resist printings under aniline black-prints.

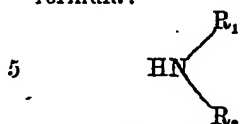
The expression "substantive azo-component" used in the description and in the claims comprises all kinds of coupling components which may be used for the preparation of azo-dyestuffs on the fibre. The components must be free from sulphonic acid and carboxylic acid groups. Coupling components of this kind are, for instance, naphthols, 2:3-hydroxynaphthoic acid arylides, compounds containing a reactive methylene group capable of coupling, such as pyrazolone compounds or β -ketocarboxylic acid arylides, for instance, the arylides of aceto-acetic acid, benzoylacetic acid, terephthaloyldiacetic acid and other acylacetic acids or diacyl-acetyl arylides, such as diacetoacetyl-benzidine or diacetoacetyl-tolidine or other condensation products from acylacetic acid esters with di- or monoamino-bases.

Other substantive azo-components are the arylides of 2:3-hydroxyanthracene-carboxylic acid, ortho-hydroxycarbazole-carboxylic acids, ortho-hydroxybenzocarbazole-carboxylic acids or the like.

These coupling components, in general, are contained in the preparations used in the present invention in the form of their alkali metal salts.

The stabilised diazo-compounds (water-soluble diazo-amino-compounds) which constitute the other components of the azo-dyestuff preparations used in the present process may be, for instance, those described in Specifications Nos. 329,353 and 320,324. They are obtainable by condensation of aromatic diazo-compounds, free from sulphonic acid and carboxylic acid groups, with primary aromatic amines which contain one or more sulpho-groups, two or more carboxyl groups or sulphy- and carboxyl groups, or with

secondary amines of the following general formula:



wherein R_1 and R_2 represent alkyl, aryl-, aralkyl- or hydroaryl- radicals which contain at least one substituent capable of rendering the components soluble in water.

Mixtures of water-soluble diazo-amino-compounds with substantive azo-components are, for instance, described in Specification No. 334,529.

The following Examples illustrate the invention:

1.) White cotton goods are printed with the following printing colour:

80 grams of the dyestuff preparation consisting of a mixture of the diazo-amino-compound from 5-chloro-2-methyl-1-aminobenzene and 4-sulpho-2-amino-1-benzoic acid with the sodium salt of 2':3'-hydroxynaphthoyl - 2 - methyl-1-aminobenzene (cf. Specification No. 334,529)

100 grams of water
30 grams of ethyl alcohol
40 grams of caustic soda solution of 38° Bé

400 grams of neutral starch tragacanth thickening

270 grams of water
50 grams of zinc white 1:1
30 grams of sodium thiosulphate

1000 grams.

After printing and drying the following printing colour is over-printed by means of an over-printing roller:

40 grams of the sodium salt of the sulphuric acid ester of the leuco-vat-dyestuff from 5:7:5':7'-tetrabromindigo

30 grams of ethylenethiodiglycol
395 grams of water of about 80° C.

400 grams of neutral starch-tragacanth thickening

30 grams of ammonia of 25 per cent. strength

30 grams of glycollic acid of 50 per cent. strength

40 grams of ammonium thiocyanate

15 grams of sodium chlorate

20 grams of ammonium vanadate I:100

1000 grams.

After over-printing and drying the material is steamed for 5 minutes in a rapid ager, rinsed and soaped at the boil.

The over-printed parts of the first printed pattern are red, and those places where the pattern of the over-printing roller had no contact with the pattern of the first printing roller appear blue.

2.) There are printed side by side on cotton goods the two printing pastes:

a) 80 grams of the dyestuff preparation consisting of a mixture of the diazo-amino-compound from 1-amino-3-chlorobenzene- and 4-sulpho-2-amino-1-benzoic acid with the sodium salt of 2':3'-hydroxynaphthoyl - 2 - methyl-1 - aminobenzene (cf. Specification No. 334,529)

100 grams of water

30 grams of alcohol

30 grams of caustic soda solution of 38° Bé

400 grams of neutral starch tragacanth thickening

50 grams of zinc white 1:1

280 grams of water

30 grams of sodium thiocyanate

1000 grams.

b) 25 grams of the dyestuff preparation consisting of a mixture of the diazo-amino-compound from 1-amino-2 - methoxy - 4 - benzoylamino - 5 - methyl - benzene and sarcosine with the sodium salt of 2':3'-hydroxynaphthoyl-aminobenzene (cf. Specification No. 334,529)

100 grams of water

30 grams of alcohol

40 grams of caustic soda solution of 38° Bé

400 grams of neutral starch tragacanth thickening

50 grams of zinc white 1:1

50 grams of magnesium oxide 1:1

30 grams of sodium thiosulphate

275 grams of water

1000 grams.

After printing and drying the goods are over-printed with the following printing colour:

40 grams of the sodium salt of the sulphuric acid ester of the leuco-vat-dyestuff from dimethoxy - dehydro - dibenzanthrone (cf. Schultz, Farbstofftabellen, 7th Edition, No. 1269).

30 grams of ethylenethiodiglycol

395 grams of water heated to about 80° C.

| | | | |
|----|---|---|-----|
| | 400 grams of neutral starch tragacanth thickening | 400 grams of neutral starch tragacanth thickening | |
| | 30 grams of ammonia of 25 per cent. strength | 280 grams of water, | |
| 5 | 30 grams of glycollic acid of 50 per cent. strength | 50 grams of zinc white 1:1 | |
| | 40 grams of ammonium thiocyanate | 30 grams of sodium thiosulphate | 70 |
| | 15 grams of sodium chlorate | | |
| | 20 grams of ammonium vanadate 1:100 | | |
| 10 | 1000 grams. | 1000 grams. | |
| | After over-printing and drying, the material is steamed for 5 minutes in a rapid ager, rinsed and soaped at the boil. | After printing and drying, the following printing colour is over-printed: | |
| 15 | The pattern of the over-printing roller appears green on those parts where there was no contact with the patterns first printed, and those places where the two patterns of the first printing rollers came in contact with the patterns of the over-printing roller, show vivid orange and violet shades corresponding with the printing pastes a) and b). | 40 grams of the ester salt of the leuco-vat-dyestuff from 5:6:7-trichlorothionaphthene-5 ¹ :7 ¹ -dichloroindol-2-indigo | 75 |
| 20 | 3.) There are printed side by side on cotton goods: | 30 grams of ethylenethiodiglycol | |
| | a) 80 grams of the dyestuff preparation consisting of a mixture of the diazo-amino-compound from 5-chloro-2-methyl-1-amino-benzene and 4-sulpho-2-amino-1-benzoic acid with the sodium salt of 2 ¹ :3 ¹ -hydroxy-naphthoyl-2-ethoxy-1-aminobenzene (cf. Specification No. 334,529). | 395 grams of water of 80° C. | 80 |
| 25 | 100 grams of water | 400 grams of neutral starch tragacanth thickening | |
| | 30 grams of ethyl alcohol | 30 grams of ammonia of 25 per cent. strength | |
| 30 | 40 grams of caustic soda solution of 38° Bé | 30 grams of glycollic acid of 50 per cent. strength | 85 |
| 35 | 400 grams of neutral starch tragacanth thickening | 40 grams of ammonium thiocyanate | |
| | 270 grams of water | 15 grams of sodium chlorate | |
| 40 | 50 grams of zinc white 1:1 | 20 grams of ammonium vanadate 1:100 | 90 |
| 45 | 30 grams of sodium thiosulphate | | |
| | 1000 grams. | 1000 grams. | |
| 50 | b) 80 grams of the dyestuff preparation obtainable according to Specification No. 328,383 and consisting of the potassium salt of the nitrosamine from 5-chloro-2-methoxy-1-amino-benzene, di-acetoacetyl-4:4 ¹ -diamino-3:3 ¹ -dimethyl-diphenyl, anhydrous sodium acetate and sodium bicarbonate | After over-printing and drying, the material is steamed for 5 minutes in a rapid ager, rinsed and soaped at the boil. | 95 |
| 55 | 100 grams of water | The pattern of the over-printing roller appears violet on those parts where there was no contact with the patterns first printed; those parts of the pattern of the over-printing roller which came in contact with the pattern produced by means of printing paste a) appear red whereas the pattern produced by means of printing paste b) appears throughout in a yellow colour. | 100 |
| 60 | 30 grams of ethyl alcohol | 4.) The following two printing colours are printed side by side on cotton goods: | |
| | 30 grams of caustic soda solution of 38° Bé | I. 80 grams of the dyestuff preparation consisting of a mixture of the diazo-amino-compound from 5-chloro-2-methyl-1-aminobenzene with 4-sulpho-2-amino-1-benzoic acid with the sodium salt of 2 ¹ :3 ¹ -hydroxynaphthoyl-2-ethoxy-1-aminobenzene (cf. Specification No. 334,529) | 105 |
| 65 | | 100 grams of water | 120 |
| | | 30 grams of alcohol | |
| | | 40 grams of caustic soda solution of 38° Bé | |
| | | 400 grams of neutral starch tragacanth thickening | 125 |
| | | 100 grams of zinc white 1:1 | |
| | | 30 grams of sodium thiosulphate | |
| | | 220 grams of water | |
| | | 1000 grams. | 130 |

| | | | | |
|----|---|---|---|-----|
| 5 | II: 40 grams of the sodium salt of the sulphuric acid ester of the leuco-vat-dyestuff from dimethoxy-dehydro-dibenzanthrone (Schultz, Farbstofftabellen, 7th Edn., No. 1269) | | 1-aminobenzene and 4-sulpho-2-amino-1-benzoic acid with the sodium salt of 2 ¹ :3 ¹ -hydroxynaphthoyl-1-amino-2-methyl-4-methoxybenzene | 70 |
| | 30 grams of ethylenethiodiglycol | 100 grams of water | | |
| | 450 grams of water of 80° C. | 30 grams of alcohol | | |
| | 400 grams of neutral starch tragacanth thickening | 30 grams of caustic soda solution of 38° Bé | | 75 |
| | 60 grams of ammonium thiocyanate | 400 grams of neutral starch tragacanth thickening | | |
| 10 | 20 grams of sodium thiosulphate | 230 grams of water | | |
| | | 50 grams of zinc white 1:1 | | |
| 15 | 1000 grams | 30 grams of sodium thiosulphate | | 80 |
| | After printing and drying, the following printing colour is over-printed | | 1000 grams. | |
| 20 | a) 85 grams of aniline salt | After printing and drying the following printing colour is over-printed: | | |
| | 5 grams of aniline oil | 40 grams of the sodium salt of the sulphuric acid ester of the leuco-vat-dyestuff from 5:7:5 ¹ :7 ¹ -tetra-bromindigo | 85 | |
| | 400 grams of neutral starch tragacanth thickening | 30 grams of ethylenethiodiglycol | | |
| 25 | b) 55 grams of potassium ferrocyanide | 395 grams of water | | 90 |
| | 250 grams of water | 400 grams of neutral starch tragacanth thickening | | |
| 30 | c) 35 grams of sodium chlorate | 30 grams of ammonia of 25 per cent. strength | | |
| | 130 grams of water | 30 grams of glycollic acid of 50 per cent. strength | | 95 |
| 35 | d) 40 grams of glycollic acid of 50 per cent. strength | 40 grams of ammonium thiocyanate | | |
| | 1000 grams. | 15 grams of sodium chlorate | | |
| 40 | a), b), c) and d) are mixed before use. | 20 grams of ammonium vanadate | | 100 |
| | After over-printing and drying the material is steamed for 5 minutes in a rapid ager, after-treated with 1 gram of potassium dichromate and 3 grams of sodium carbonate, rinsed and soaped at the boil. | | 1:100 | |
| 45 | The aniline black is developed on those parts of the pattern of the over-printing roller which had no contact with the patterns first printed; and those parts where the pattern first printed with printing paste I came in contact with the pattern of the over-printing roller show scarlet red shades, whilst those parts where the pattern first printed with printing paste II came in contact with the pattern of the over-printing roller appear green. | | 1000 grams. | |
| | 5). The following printing colour is printed on cotton goods: | | After overprinting the material is steamed for 5 minutes, rinsed and soaped at the boil. | |
| 50 | 10 grams of the dyestuff preparation consisting of a mixture of the sodium salt of the nitrosamine from 4-chloro-2-methyl-1-aminobenzene with the sodium salt of 2 ¹ :3 ¹ -hydroxynaphthoyl-1-amino-2-methyl-4-methoxybenzene | The pattern of the over-printing roller appears blue on those parts where there was no contact with the pattern first printed, and those places where the pattern of the first printing roller came in contact with the pattern of the over-printing roller appear dark red; furthermore, the whole of the first printed pattern shows a pink shade as the mixture of nitrosamine and substantive azo-component in the first printing colour is wholly developed by the steaming operation. | | 105 |
| | 70 grams of the dyestuff preparation consisting of a mixture of the diazo-amino-compound from 4-chloro-2-methyl- | Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:— | | 110 |
| 55 | 1. Process of producing conversion effects on textile materials by printing on the material a printing paste containing a mixture of a substantive azo-component free from sulphonic or carboxylic acid groups with a water-soluble diazo-amino-compound, a quantity of alkali necessary for dissolving the dyestuff component, a | | 125 | |
| | | | 130 | |

resist to ester salts of leuco-vat-dyestuffs and, if required, a small quantity of a reducing agent of mild action, thereupon over-printing in a different pattern with a
5 printing paste containing an ester salt of a leuco-vat-dyestuff, an oxidising agent, such as sodium chlorate, an agent yielding a non-volatile acid, for instance an ammonium salt of a non-volatile acid,
10 such as thiocyanic acid, glycollic acid, oxalic acid, lactic acid, citric acid or tartaric acid, or diethyltartrate or the like, or an easily dissociating metal salt of a non-volatile acid, such as, for instance, a
15 sulphate of magnesium, zinc, aluminium or the like, or a mixture of the said substances which yield non-volatile acid and furthermore an oxidation accelerator, such as ammonium vanadate, subjecting the
20 material thus treated to a steaming operation, washing and soaping.

2. A modification of the process according to claim 1, wherein there is substituted for the ester salt of a leuco-vat-dye-

stuff and for the resist therefor an aniline 25 black or similar preparation and a resist therefor respectively, and wherein, if desired, instead of the agent yielding a non-volatile acid or easily dissociating metal salt in the printing paste for over-printing 30 there may be used a free non-volatile organic acid or a feeble non-volatile inorganic acid.

3. Process of producing conversion effects on textile materials substantially as 35 described with reference to any of the Examples herein.

4. Conversion effects when prepared or produced on textile materials by the particular process described and ascertained 40 herein or by any process which is an obvious chemical equivalent thereof.

Dated this 14th day of July, 1933.

ABEL & IMRAY,

30, Southampton Buildings, London.

W.C.2,

Agents for the Applicants.